

## **CATALYST PRETREATMENT WITH ALDEHYDE IN AN OXYGENATE TO OLEFINS REACTION SYSTEM**

### **Field of the Invention**

**[0001]** This invention relates to processes for converting oxygenates to olefins. In particular, this invention relates to processes for converting oxygenates to olefins that include a step of pretreating catalyst used in the conversion reaction.

### **Background of the Invention**

**[0002]** Methanol is used as a feed stock for a variety of chemical manufacturing processes. One process that is more recently being developed is the conversion of methanol to olefin products, particularly products containing the olefins ethylene and propylene. The olefins produced from the methanol conversion process are of suitable quality to be used in polymer manufacturing processes. Of particular commercial concern in the methanol conversion process, however, is whether sufficient quantities of light olefins (i.e., ethylene and propylene) can be produced.

**[0003]** U.S. Patent No. 4,677,242 (Kaiser) describes the use of a silicoaluminophosphate (SAPO) molecular sieve catalyst for converting various oxygenates, such as methanol, to olefins. According to the patent, the SAPO catalyst is an extremely efficient catalyst for the conversion of oxygenates to light olefin products when the feed is converted in the presence of a diluent. The diluent used has an average kinetic diameter larger than the pores of the SAPO molecular sieve. The selected SAPO molecular sieves have pores that an average kinetic diameter characterized such that the adsorption capacity (as measured by the standard McBain-Bakr gravimetric adsorption method using given adsorbate molecules) shows adsorption of oxygen (average kinetic diameter of about 3.36 angstroms) and negligible adsorption of isobutane (average kinetic diameter of about 5.0 angstroms).

**[0004]** U.S. Patent No. 6,046,372 (Brown et al.) discloses another method of converting methanol to light olefins. The method incorporates the use of medium pore zeolite molecular sieves, particularly medium pore ZSM type

zeolites, in converting methanol and/or dimethyl ether to light olefin. Light olefin production is aided by the use of an aromatic compound as a co-feed. The aromatic compound has a critical diameter less than the pore size of the catalyst, and is capable of alkylation by the methanol and/or dimethyl ether. Ethylene product selectivity is believed to be derived from the back-cracking of ethyl-aromatic intermediates. The formation of the ethyl-aromatic intermediates is believed to be facilitated by a mechanism in which the aromatic compound effectively acts as a catalyst in the conversion of two molecules of methanol to one molecule of ethylene.

**[0005]** U.S. Patent No. 6,051,746 (Sun et al.) also describes a method for increasing light olefin selectivity in the conversion of oxygenates using a small pore molecular sieve catalyst. The selectivity is increased by exposing a catalyst to a modifier before or during the conversion reaction. The modifier is a polynuclear aromatic having at least three interconnected ring structures, with each ring structure having at least 5 ring members. It is adsorbed onto the catalyst prior to or simultaneously with the introduction of feed.

**[0006]** U.S. Patent No. 6,137,022 (Kuechler et al.) is to a process for increasing the selectivity of a reaction to convert oxygenates to olefins. The process involves contacting the oxygenate in a reaction zone containing 15 volume percent or less of a catalyst comprising SAPO molecular sieve, and maintaining conversion of the feedstock between 80% and 99% under conditions effective to convert 100% of the feedstock when the reaction zone contains at least 33 volume percent of the molecular sieve material. The process is considered to be beneficial in maximizing the production of ethylene and/or propylene, and to minimize the production of undesired products.

**[0007]** U.S. Patent No. 6,225,254 (Janssen et al.) is directed to a method of maintaining acid catalyst sites of a SAPO molecular sieve catalyst. According to the patent, catalyst sites are lost when exposed to a moisture-containing environment. In order to maintain the catalyst sites, and thereby preserve catalyst activity, template-containing SAPO molecular sieves are heated in an oxygen depleted environment under conditions effective to provide an integrated catalyst life that is greater than that obtained in a non-oxygen depleted environment.

**[0008]** U.S. Patent No. 6,436,869 (Searle et al.) is directed to a method of obtaining olefin product high in ethylene and/or propylene content, while reducing the amount of any one or more of C<sub>1</sub>-C<sub>4</sub> paraffin by-products, and to reduce the amount of coke deposits on the catalyst during the reaction. The method is accomplished by providing a catalyst that comprises SAPO crystals, a binder comprising ALPO crystals, and nickel, cobalt and/or iron, wherein the catalyst does not contain significant amounts of amorphous binder, but rather contains crystalline SLPO.

**[0009]** U.S. Patent No. 6,437,208 (Kuechler et al.) discloses a method for making olefin product from an oxygenate-containing feedstock. In the method, a SAPO molecular sieve catalyst is contacted with the oxygenate-containing feedstock in a reactor at an average catalyst feedstock exposure index of at least 1.0. The average catalyst feedstock exposure index is the total weight of oxygenate plus hydrocarbon fed to the reactor divided by the total weight of fresh and regenerated SAPO molecular sieve (i.e., excluding binder, inerts, etc., of the catalyst composition) sent to the reactor, both total weights measured over the same period of time. The method is shown to be effective in maintaining a high ethylene and propylene selectivity.

**[0010]** WO 01/62382 A2 (ExxonMobil Chemical Patents Inc.) discloses that selectivity to ethylene and propylene can be increased by pretreating a SAPO molecular sieve to form an integrated hydrocarbon co-catalyst within the framework of the molecular sieve prior to contacting with oxygenate feed. Acetone, methanol, propene, butene, pentene and hexene are given as examples of pretreatment compounds capable of forming an integrated hydrocarbon co-catalyst. The conditions for pretreatment include pretreating at a lower temperature relative to the reaction temperature. A preferred pretreatment vessel is an auxiliary fluidized bed reactor system associated with the oxygenate conversion reactor.

**[0011]** In spite of the recent technological advances in converting oxygenates to olefins, there remains a need to further increase the quantity of light olefins in the conversion product. In particular, there remains a need to increase product selectivity to ethylene and propylene, and particularly to ethylene.

**Summary of the Invention**

**[0012]** This invention provides processes for converting oxygenates to olefins that show enhanced selectivity to ethylene and/or propylene. The processes involve pretreating the conversion catalyst with an aldehyde in a pretreatment zone.

**[0013]** In one aspect, the invention provides a process for making an olefin product from an oxygenate feed. The process includes a step of contacting a metalloaluminophosphate molecular sieve having a porous framework structure with a C<sub>2</sub>-C<sub>4</sub> aldehyde composition in a pretreatment zone to form an integrated hydrocarbon co-catalyst within the porous framework. The metalloaluminophosphate molecular sieve containing the integrated hydrocarbon co-catalyst is contacted with an oxygenate in an oxygenate conversion zone to convert the oxygenate to olefin product.

**[0014]** In another aspect, there is provided a process for making an olefin product and polyolefin from an oxygenate feed. The process includes a step of contacting a metalloaluminophosphate molecular sieve having a porous framework structure with a C<sub>2</sub>-C<sub>4</sub> aldehyde composition in a pretreatment zone to form an integrated hydrocarbon co-catalyst within the porous framework. The metalloaluminophosphate molecular sieve containing the integrated hydrocarbon co-catalyst is contacted with an oxygenate in an oxygenate conversion zone to convert the oxygenate to olefin product, an at least one olefin in the olefin product is contacted with a polyolefin forming catalyst to form polyolefin.

**[0015]** In one embodiment of the invention, the molecular sieve contacting the aldehyde composition in a pretreatment zone has a carbon content of not greater than 2 wt %, based on total weight of the molecular sieve prior to contact with the aldehyde. Preferably, the molecular sieve contacting the aldehyde composition in a pretreatment zone has a carbon content of not greater than 1.5 wt %, more preferably not greater than 1 wt %, and most preferably not greater than 0.5 wt %, based on total weight of the molecular sieve prior to contact with the aldehyde.

**[0016]** In another embodiment, the molecular sieve containing the integrated hydrocarbon co-catalyst in the oxygenate removal zone has a

hydrocarbon content of at least 0.1 wt %, based on total weight of the molecular sieve, prior to contacting the oxygenate. Preferably, the molecular sieve containing the integrated hydrocarbon co-catalyst in the oxygenate removal zone has a hydrocarbon content of at least 1 wt %, more preferably at least 5 wt %, based on total weight of the molecular sieve, prior to contacting the oxygenate.

**[0017]** In yet another embodiment, the molecular sieve contacts the aldehyde composition in the pretreatment zone at a temperature that is lower than that at which the molecular sieve contacts the oxygenate in the oxygenate removal zone. Preferably, the molecular sieve contacts the aldehyde composition in the pretreatment zone at temperature that is at least 10°C lower, more preferably at least 25°C lower, and most preferably at least 50°C lower than that at which the molecular sieve of step b) contacts the oxygenate in the oxygenate removal zone.

**[0018]** In another embodiment, the molecular sieve contacts the aldehyde composition in the pretreatment zone at a WHSV that is lower than that at which the molecular sieve of contacts the oxygenate. Preferably, the molecular sieve contacts the aldehyde composition in the pretreatment zone at WHSV that is at least 5 hr<sup>-1</sup> lower, more preferably at least 10 hr<sup>-1</sup> lower, and most preferably at least 15 hr<sup>-1</sup> lower than that at which the molecular sieve contacts the oxygenate.

**[0019]** In a particular embodiment, the molecular sieve contacts the aldehyde composition in the pretreatment zone at an aldehyde to molecular sieve weight ratio of from 0.01:1 to 3:1. In another, the molecular sieve contacts the aldehyde composition in the pretreatment zone at an aldehyde to molecular sieve weight ratio of from 0.05:1 to 2:1 or from 0.1:1 to 1:1.

**[0020]** The metalloaluminophosphate molecular sieve is desirably silicoaluminophosphate molecular sieve. In one embodiment, the metallaluminophosphate molecular sieve is selected from the group consisting of SAPO-5, SAPO-8, SAPO-11, SAPO-16, SAPO-17, SAPO-18, SAPO-20, SAPO-31, SAPO-34, SAPO-35, SAPO-36, SAPO-37, SAPO-40, SAPO-41, SAPO-42, SAPO-44, SAPO-47, SAPO-56, AIPO-5, AIPO-11, AIPO-18, AIPO-31, AIPO-34, AIPO-36, AIPO-37, AIPO-46, metal containing molecular sieves thereof, and combinations thereof.

[0021] The aldehyde composition can contain other compounds in addition to the one or more aldehyde compounds. For example, the aldehyde composition contacting the molecular sieve in the pretreatment zone comprises less than 50 wt % aldehyde, based on total weight of the composition. In one embodiment, the aldehyde composition contacting the molecular sieve in the pretreatment zone comprises from 0.5 wt % to 45 wt % aldehyde, based on total weight of the composition.

[0022] A variety of aldehydes are effective in the invention. For example, the aldehyde composition can contain acetaldehyde, propionaldehyde, butyraldehyde, or a combination thereof. Typically, a greater content of aldehyde can be separated and recovered from an oxygenate conversion product, when the oxygenate conversion zone of that process converts less than 100% of the oxygenate to olefin product.

#### **Brief Description of the Drawings**

[0023] Examples of various embodiments of this invention are shown in the attached Figures, wherein:

[0024] FIG. 1 is a schematic showing separation of an aldehyde stream from the C<sub>2</sub>, C<sub>3</sub> and C<sub>4</sub> components of the olefin stream; and

[0025] FIG. 2 is a schematic showing separation of an aldehyde stream from the C<sub>2</sub>, C<sub>3</sub> and C<sub>4</sub> components of the olefin stream using an extractant to aid in removing the aldehyde compounds.

#### **Detailed Description of the Invention**

##### **I. Pretreatment of Molecular Sieve with Aldehyde**

[0026] This invention is directed to processes for making olefin product from an oxygenate feed. The processes include a step of pretreating a fresh or regenerated metalloaluminophosphate molecular sieve, which is low in carbon content, with an aldehyde. The aldehyde forms a hydrocarbon co-catalyst within the pore structure of the molecular sieve, and the pretreated molecular sieve containing the co-catalyst is used to convert oxygenate to an olefin product.

[0027] Only a relatively low amount of aldehyde is needed to provide a molecular sieve or catalyst containing molecular sieve that effectively converts an

oxygenate compound to olefin product, with a high selectivity to ethylene and/or propylene. This means that a relatively low amount of aldehyde can be used to effectively pretreat the molecular sieve (i.e., form a co-catalyst within the molecular sieve) such that subsequent contact of the pretreated molecular sieve with oxygenate will convert a significant amount of the oxygenate directly to ethylene and propylene (i.e., will convert at a high selectivity to ethylene and propylene). The resulting olefin product, will, therefore, contain a significant amount of ethylene and propylene, with relatively low amounts of undesired by-products.

## II. Types of Molecular Sieve

**[0028]** The molecular sieves that are included in the catalyst or catalyst mixtures used in the conversion of oxygenates to olefins in this invention are preferably metalloaluminophosphate molecular sieves that have a molecular framework that include  $[\text{AlO}_4]$  and  $[\text{PO}_4]$  tetrahedral units, such as metal containing aluminophosphates (AIPO). In one embodiment, the metalloaluminophosphate molecular sieves include  $[\text{AlO}_4]$ ,  $[\text{PO}_4]$  and  $[\text{SiO}_4]$  tetrahedral units, such as silicoaluminophosphates (SAPO).

**[0029]** Various silicon, aluminum, and phosphorus based molecular sieves and metal-containing derivatives thereof have been described in detail in numerous publications including for example, U.S. Patent No. 4,567,029 (MeAPO where Me is Mg, Mn, Zn, or Co), U.S. Patent No. 4,440,871 (SAPO), European Patent Application EP-A-0 159 624 (ELAPSO where El is As, Be, B, Cr, Co, Ga, Ge, Fe, Li, Mg, Mn, Ti or Zn), U.S. Patent No. 4,554,143 (FeAPO), U.S. Patents No. 4,822,478, 4,683,217, 4,744,885 (FeAPSO), EP-A-0 158 975 and U.S. Patent No. 4,935,216 (ZnAPSO, EP-A-0 161 489 (CoAPSO), EP-A-0 158 976 (ELAPO, where EL is Co, Fe, Mg, Mn, Ti or Zn), U.S. Patent No. 4,310,440 (AIPO<sub>4</sub>), EP-A-0 158 350 (SENAPSO), U.S. Patent No. 4,973,460 (LiAPSO), U.S. Patent No. 4,789,535 (LiAPO), U.S. Patent No. 4,992,250 (GeAPSO), U.S. Patent No. 4,888,167 (GeAPO), U.S. Patent No. 5,057,295 (BAPSO), U.S. Patent No. 4,738,837 (CrAPSO), U.S. Patents Nos. 4,759,919, and 4,851,106 (CrAPO), U.S. Patents Nos. 4,758,419, 4,882,038, 5,434,326 and 5,478,787 (MgAPSO), U.S. Patent No. 4,554,143 (FeAPO), U.S. Patent No. 4,894,213 (AsAPSO), U.S. Patent

No. 4,913,888 (AsAPO), U.S. Patents Nos. 4,686,092, 4,846,956 and 4,793,833 (MnAPSO), U.S. Patents Nos. 5,345,011 and 6,156,931 (MnAPO), U.S. Patent No. 4,737,353 (BeAPSO), U.S. Patent No. 4,940,570 (BeAPO), U.S. Patents Nos. 4,801,309, 4,684,617 and 4,880,520 (TiAPSO), U.S. Patents Nos. 4,500,651, 4,551,236 and 4,605,492 (TiAPO), U.S. Patents No. 4,824,554, 4,744,970 (CoAPSO), U.S. Patent No. 4,735,806 (GaAPSO) EP-A-0 293 937 (QAPSO, where Q is framework oxide unit  $[QO_2]$ ), as well as U.S. Patents Nos. 4,567,029, 4,686,093, 4,781,814, 4,793,984, 4,801,364, 4,853,197, 4,917,876, 4,952,384, 4,956,164, 4,956,165, 4,973,785, 5,241,093, 5,493,066 and 5,675,050, all of which are herein fully incorporated by reference. Other molecular sieves include those described in R. Szostak, Handbook of Molecular Sieves, Van Nostrand Reinhold, New York, New York (1992), which is herein fully incorporated by reference.

**[0030]** The more preferred molecular sieves are SAPO molecular sieves, and metal-substituted SAPO molecular sieves. Suitable metal substituents are alkali metals of Group IA of the Periodic Table of Elements, an alkaline earth metals of Group IIA of the Periodic Table of Elements, a rare earth metals of Group IIIB, including the Lanthanides: lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutetium; and scandium or yttrium of the Periodic Table of Elements, transition metals of Groups IVB, VB, VIB, VIIB, VIIIB, and IB of the Periodic Table of Elements and mixtures of any of these metal species. In one embodiment, the metal is selected from the group consisting of Co, Cr, Cu, Fe, Ga, Ge, Mg, Mn, Ni, Sn, Ti, Zn and Zr, and mixtures thereof. The metal atoms may be inserted into the framework of a molecular sieve through a tetrahedral unit, such as  $[MeO_2]$ , and carry a net charge depending on the valence state of the metal substituent. For example, in one embodiment, when the metal substituent has a valence state of +2, +3, +4, +5, or +6, the net charge of the tetrahedral unit is between -2 and +2.

**[0031]** In one embodiment, the metalloaluminophosphate molecular sieve is represented, on an anhydrous basis, by the formula:





**[0032]** wherein R represents at least one templating agent, preferably an organic templating agent; m is the number of moles of R per mole of  $(M_xAl_yP_z)O_2$  and m has a value from 0 to 1, preferably 0 to 0.5, and most preferably from 0 to 0.3; x, y, and z represent the mole fraction of Al, P and M as tetrahedral oxides, where M is a metal selected from the group consisting of Group IA, IIA, IB, IIIB, IVB, VB, VIB, VIIB, VIIIB and Lanthanide's of the Periodic Table of Elements. Preferably M is one or more metals selected from the group consisting of Si, Co, Cr, Cu, Fe, Ga, Ge, Mg, Mn, Ni, Sn, Ti, Zn and Zr. In an embodiment, m is greater than or equal to 0.2, and x, y and z are greater than or equal to 0.01. In another embodiment, m is greater than 0.1 to about 1, x is greater than 0 to about 0.25, y is in the range of from 0.4 to 0.5, and z is in the range of from 0.25 to 0.5, more preferably m is from 0.15 to 0.7, x is from 0.01 to 0.2, y is from 0.4 to 0.5, and z is from 0.3 to 0.5.

**[0033]** In one embodiment of the invention, the metalloaluminophosphate molecular sieves are silicoaluminophosphate molecular sieves, containing silicon and aluminum. Desirably, the metalloaluminophosphate molecular sieves of this invention are silicoaluminophosphate molecular sieves that contain Si and Al, at a Si/Al ratio of not greater than about 0.5, preferably not greater than about 0.3, more preferably not greater than about 0.2, still more preferably not greater than about 0.15, and most preferably not greater than about 0.1. In another embodiment, the Si/Al ratio is sufficiently high to allow for increased catalytic activity of the molecular sieve. Preferably, the metalloaluminophosphate molecular sieves are silicoaluminophosphate molecular sieves that contain Si and Al at a ratio of at least about 0.005, more preferably at least about 0.01, and most preferably at least about 0.02.

**[0034]** Non-limiting examples of SAPO and AIPO molecular sieves useful herein include one or a combination of SAPO-5, SAPO-8, SAPO-11, SAPO-16, SAPO-17, SAPO-18, SAPO-20, SAPO-31, SAPO-34, SAPO-35, SAPO-36, SAPO-37, SAPO-40, SAPO-41, SAPO-42, SAPO-44, SAPO-47, SAPO-56, AIPO-5, AIPO-11, AIPO-18, AIPO-31, AIPO-34, AIPO-36, AIPO-37, AIPO-46, and metal containing molecular sieves thereof. Of these, particularly useful molecular sieves are one or a combination of SAPO-18, SAPO-34, SAPO-35,

SAPO-44, SAPO-56, AIPO-18, AIPO-34 and metal containing derivatives thereof, such as one or a combination of SAPO-18, SAPO-34, AIPO-34, AIPO-18, and metal containing derivatives thereof, and especially one or a combination of SAPO-34, AIPO-18, and metal containing derivatives thereof.

**[0035]** In an embodiment, the molecular sieve is an intergrowth material having two or more distinct crystalline phases within one molecular sieve composition. In particular, intergrowth molecular sieves are described in U.S. Patent Application Publication No. 2002-0165089 and International Publication No. WO 98/15496, published April 16, 1998, both of which are herein fully incorporated by reference. For example, SAPO-18, AIPO-18 and RUW-18 have an AEI framework-type, and SAPO-34 has a CHA framework-type. Thus, the molecular sieve used herein may comprise at least one intergrowth phase of AEI and CHA framework-types, especially where the ratio of CHA framework-type to AEI framework-type, as determined by the DIFFaX method disclosed in U.S. Patent Application Publication No. 2002-0165089, is greater than 1:1.

**[0036]** Various methods for synthesizing molecular sieves or modifying molecular sieves are described in U.S. Patent No. 5,879,655 (controlling the ratio of the templating agent to phosphorus), U.S. Patent No. 6,005,155 (use of a modifier without a salt), U.S. Patent No. 5,475,182 (acid extraction), U.S. Patent No. 5,962,762 (treatment with transition metal), U.S. Patent Nos. 5,925,586 and 6,153,552 (phosphorus modified), U.S. Patent No. 5,925,800 (monolith supported), U.S. Patent No. 5,932,512 (fluorine treated), U.S. Patent No. 6,046,373 (electromagnetic wave treated or modified), U.S. Patent No. 6,051,746 (polynuclear aromatic modifier), U.S. Patent No. 6,225,254 (heating template), PCT WO 01/36329 published May 25, 2001 (surfactant synthesis), PCT WO 01/25151 published April 12, 2001 (staged acid addition), PCT WO 01/60746 published August 23, 2001 (silicon oil), U.S. Patent Application Publication No. 20020055433 published May 9, 2002 (cooling molecular sieve), U.S. Patent No. 6,448,197 (metal impregnation including copper), U.S. Patent No. 6,521,562 (conductive microfilter), and U.S. Patent Application Publication No. 20020115897 published August 22, 2002 (freeze drying the molecular sieve), which are all herein fully incorporated by reference.

**[0037]** In general, molecular sieve catalyst is also referred to as formulated molecular sieve catalyst. The formulated catalyst optionally contains binder and matrix materials. Conventionally, formulated catalyst is made by mixing together molecular sieve crystals (which includes template) and a liquid, optionally with matrix material and/or binder, to form a slurry. The slurry is then dried (i.e., liquid is removed), without completely removing the template from the molecular sieve. Since this dried molecular sieve catalyst includes template, it has not been activated, and is considered a preformed catalyst. However, the preformed catalyst must be activated before use, and this invention provides appropriate methods to protect the activated catalyst from significant deactivation.

**[0038]** The liquid used to form the slurry can be any liquid conventionally used in formulating molecular sieve catalysts. Non-limiting examples of suitable liquids include water, alcohol, ketones, aldehydes, esters, or a combination thereof. Water is a preferred liquid.

**[0039]** Matrix materials are optionally included in the slurry used to make the formulated molecular sieve catalyst of this invention. Such materials are typically effective as thermal sinks assisting in shielding heat from the catalyst composition, for example, during regeneration. They can further act to densify the catalyst composition, increase catalyst strength such as crush strength and attrition resistance, and to control the rate of conversion in a particular process. Non-limiting examples of matrix materials include one or more of: rare earth metals, metal oxides including titania, zirconia, magnesia, thoria, beryllia, quartz, silica or sols, and mixtures thereof; for example, silica-magnesia, silica-zirconia, silica-titania, silica-alumina and silica-alumina-thoria.

**[0040]** In one embodiment, matrix materials are natural clays, such as those from the families of montmorillonite and kaolin. These natural clays include kaolins known as, for example, Dixie, McNamee, Georgia and Florida clays. Non-limiting examples of other matrix materials include: halloysite, kaolinite, dickite, nacrite, or anauxite. Optionally, the matrix material, preferably any of the clays, are calcined, acid treated, and/or chemical treated before being used as a slurry component. Under the optional calcination treatment, the matrix

material will still be considered virgin material as long as the material has not been previously used in a catalyst formulation.

**[0041]** In a particular embodiment, the matrix material is a clay or a clay-type composition, preferably a clay or clay-type composition having a low iron or titania content, and most preferably the matrix material is kaolin. Kaolin has been found to form a pumpable, high solid content slurry; it has a low fresh surface area, and it packs together easily due to its platelet structure.

**[0042]** Binders are also optionally included in the slurry used to make the formulated molecular sieve catalysts of this invention. Such materials act like glue, binding together the molecular sieve crystals and other materials, to form a formulated catalyst composition. Non-limiting examples of binders include various types of inorganic oxide sols such as hydrated aluminas, silicas, and/or other inorganic oxide sols. In one embodiment of the invention, the binder is an alumina-containing sol, preferably aluminium chlorohydrate. Upon calcining, the inorganic oxide sol, is converted into an inorganic oxide matrix component, which is particularly effective in forming a hardened molecular sieve catalyst composition. For example, an alumina sol will convert to an aluminium oxide matrix following heat treatment.

**[0043]** The molecular sieve crystals are mixed with liquid, and the optional matrix material and/or binder, using conventional techniques to form a slurry. The components can be mixed in any order, and the mixture is thoroughly stirred to form the slurry. The more thorough the stirring, the better the consistency of the slurry.

**[0044]** Liquid is removed from the slurry containing the molecular sieve crystals to form a preformed molecular sieve catalyst. Preferably, the slurry is fed to a forming unit that produces the preformed molecular sieve catalyst composition. The forming unit may be any conventional unit, such as a spray dryer, pelletizer, extruder, etc. In a preferred embodiment, the forming unit is spray dryer, which removes water from the slurry by a heating or drying process. Preferably, the forming unit is maintained at a temperature sufficient to remove a majority of the liquid from the slurry.

[0045] The molecular sieve material is activated by removing the template from the preformed molecular sieve catalyst composition so as to expose the active catalytic sites to the environment. The template can be removed by any conventional technique, including for example by elution methods or by heating such as calcining. The molecular sieve crystals themselves can be activated for immediate catalytic use or for storing or transporting prior to use. However, it is preferred that the molecular sieves be formulated into a preformed catalyst, then activated by calcining. The formulated product generally provides the most effective particle size and hardness for commercial scale equipment.

### III. Aldehyde Composition

[0046] The aldehyde that is used to pretreat the molecular sieve composition is an aldehyde compound that has a kinetic diameter less than the average pore opening of the molecular sieve. Desirably, the aldehyde is a C<sub>2</sub>-C<sub>4</sub> aldehyde. The aldehyde is generally selected from the group consisting of acetaldehyde, propionaldehyde, butyraldehyde, and any combination thereof. Preferably, the aldehyde is acetaldehyde, propionaldehyde, or a combination thereof.

[0047] The aldehyde is contacted with the molecular sieve so as to form an integrated hydrocarbon co-catalyst within the pore structure of the molecular sieve. The integrated hydrocarbon co-catalyst is preferably a single ring aromatic compound. More preferably, the integrated hydrocarbon co-catalyst is a benzene-based compound. Still more preferably, the integrated hydrocarbon co-catalyst is identified by Solid State Nuclear Magnetic Resonance (SSNMR) spectra comprising a peak in the 18 ppm to 40 ppm region and a peak in the 120 ppm to 150 ppm region. Alternatively, the intensity of the peak in the 18 ppm to 40 ppm region is negligible, with a single peak near 128 ppm. In one embodiment, the molecular sieve exhibits a ratio in the intensity of the peak in the 18 ppm to 40 ppm region to the intensity of the peak in the 120 ppm to 150 ppm region of not greater than about 1.0. More preferably, the molecular sieve exhibits a ratio in the intensity of the peak in the 18 ppm to 40 ppm region to the intensity of the peak in the 120 ppm to 150 ppm region of between about 0.15 and 0.7.

**[0048]** An important advantage of using the aldehyde compositions of this invention to pretreat the molecular sieve is that a relatively small amount of aldehyde components are needed to provide a substantial increase in selectivity to ethylene and propylene content in the olefin product. An effective amount of aldehyde as a pretreatment agent will result in an increase of at least 2 wt % ethylene and propylene in the olefin product. Preferably, the amount of aldehyde applied as a pretreatment agent will result in an increase of at least 3 wt % ethylene and propylene in the olefin product, more preferably at least 4 wt % ethylene and propylene in the olefin product.

**[0049]** In one embodiment, the molecular sieve that is to be pretreated contacts the aldehyde composition in a pretreatment zone at an aldehyde to molecular sieve weight ratio of from 0.01:1 to 3:1. This ratio is based on total amount of aldehyde compounds in the composition, and on total weight of molecular sieve, excluding any other non-molecular sieve components that may be present in a formulated molecular sieve composition, including matrix, binder, etc. Preferably, the molecular sieve that is to be pretreated contacts the aldehyde composition at an aldehyde to molecular sieve weight ratio of from 0.05:1 to 2:1, more preferably from 0.1:1 to 1:1, and most preferably from 0.15:1 to 0.5:1.

**[0050]** The advantages of using aldehyde compounds as a pretreatment agent are readily achieved in compositions containing the aldehyde compounds in a minor amount (i.e., less than 50 wt %). In particular, the aldehyde compounds can be mixed with other oxygenated hydrocarbon compounds and used as a pretreatment agent. Oxygenated hydrocarbon compounds that act as solvents or absorbents for the aldehydes are particularly useful, particularly oxygenated hydrocarbons having a boiling point at 1 atm. of from about 0°C to about 100°C, more particularly a boiling point at 1 atm. of from about 5°C to about 90°C.

**[0051]** Oxygenated hydrocarbons can also be included in a mixture with the aldehydes. Such hydrocarbons are preferably those that have a boiling point at 1 atm. of from about 50°C to about 90°C. Preferred examples of such hydrocarbons include methanol and acetone. Such compounds are particularly useful in absorbing aldehydes, particularly the C<sub>2</sub>-C<sub>4</sub> aldehydes, from other hydrocarbon streams.

**[0052]** In one embodiment, the aldehyde containing stream that is used as the pretreatment stream comprises from about 0.5 wt % to about 45 wt % total aldehyde, based on total weight of the pretreatment stream. Preferably, the pretreatment stream comprises from about 1 wt % to about 25 wt % total aldehyde, more preferably from about 2 wt % to about 15 wt % total aldehyde, based on total weight of the pretreatment stream.

**[0053]** Methanol is particularly useful in recovering relatively small amounts of aldehydes from other hydrocarbon streams such as alkane or alkene streams, particularly from low molecular weight olefin streams such as streams containing predominantly C<sub>2</sub>-C<sub>4</sub> olefins. In one embodiment, the aldehyde containing stream that is used as the pretreatment stream comprises a majority of methanol (i.e., greater than 50 wt %), based on total weight of the pretreatment stream. In another embodiment, the aldehyde containing stream that is used as the pretreatment stream comprises from about 50 wt % to about 85 wt % methanol, based on total weight of the pretreatment stream. In yet another embodiment, the aldehyde containing stream comprises from about 55 wt % to about 75 wt % methanol, based on total weight of the pretreatment stream.

**[0054]** Acetone, when present in the pretreatment stream, is optionally included. In one embodiment, the pretreatment stream comprises from about 1 wt % to about 20 wt % acetone, based on total weight of the pretreatment stream. In another embodiment, the pretreatment stream comprises from about 1.5 wt % to about 10 wt % acetone, and in another embodiment, from about 2 wt % to about 8 wt % acetone, based on total weight of the pretreatment stream.

**[0055]** The aldehyde pretreatment compounds of this invention are obtained, in one embodiment, from an olefin product stream of an oxygenate to olefin reaction process. Aldehydes are considered by-products in the oxygenate to olefins reaction process, and are removed from the product stream using any conventional means capable of removing such by-products to the appropriate level. Conventional distillation techniques are particularly desirable methods, and temperatures and pressures effective for separating the by-product aldehydes, particularly C<sub>2</sub>-C<sub>4</sub> aldehydes, from the light olefin containing product according to boiling point are used to separate the compounds. In this case, light olefins refers

to one or more of ethylene, propylene and butylene. Preferably a majority of the aldehyde compounds are separated from the ethylene, propylene, and butylene containing product streams.

**[0056]** In order to obtain a particularly high degree of separation between the heavier aldehyde compounds from ethylene, propylene and/or butylene, absorption or extractive distillation can be optionally used. Extractive distillation differs from conventional distillation to the extent that the ethylene, propylene and/or butylene components of the olefin product stream are distilled from the aldehydes using an extractant to aid the distillation process. Absorption differs from the extractive distillation in that an extractant is used to aid in the separation of the aldehydes, but no additional heat is added to the system as in distillation.

**[0057]** Absorption and extractive distillation are carried out using a vessel or tower having internal packing or trays that creates a temperature difference from top to bottom of the tower. The upper portion of the tower is the cooler portion, and higher volatile components in the feed exit from the top of the tower.

**[0058]** An extractant or solvent is added to the extractive distillation vessel or tower or the absorber so as to enhance or suppress the volatility of the aldehyde compounds, or other oxygenated hydrocarbons that can also be present, relative to the light olefin products. This makes it easier to separate the heavier aldehydes and oxygenated hydrocarbons from the light olefins.

**[0059]** Absorbents or extractants which can be used in this invention are preferably liquids at 1 atm. These extractants are preferably oxygenated hydrocarbon compounds that act as solvents or absorbents for the aldehyde compounds. Preferably, the extractants have an average boiling point at 1 atm of not greater than 120°C, more particularly not greater than 110°C, and most particularly not greater than 100°C. Average boiling point, as defined herein, takes into account the boiling point of each compound in the absorbent on a weight average basis. For example, an absorbent containing 90 wt.% of a compound having a boiling point of 100 degrees and 10 wt.% of a compound having a boiling point of 200 degrees would have an average boiling point of 110 degrees.



**[0060]** The extractants or absorbents are also desirably polar compositions effective at removing other oxygenated hydrocarbons in the olefin product stream that are also effective as pretreatment agents. Such extractants or absorbents include, but are not limited to, compounds such as water, monohydric alcohols, polyhydric alcohols, or mixtures thereof. Preferred monohydric alcohols include methanol, ethanol and propanol. Preferred polyhydric alcohols include glycols. Preferred glycols include ethylene glycol and tri-ethylene glycol. It is desirable that the extractant or absorbent contain at least about 75 wt.% monohydric alcohol and/or polyhydric alcohol, preferably at least about 85 wt.%, more preferably at least about 90 wt.%, and most preferably at least about 95 wt.%. Methanol is most preferred as the extractant or absorbent in this invention.

**[0061]** The extractive distillation process is particularly effective for not only separating aldehydes from the lighter olefins, ethylene, propylene and butylene, but also in removing very low concentrations of oxygenate hydrocarbons present in an olefin stream. In one embodiment of the invention, extractant is added at an upper region of an extractive distillation column, and the olefin product that contains the aldehyde is added at a side region of the column. Separated ethylene, propylene and/or butylene is recovered from the column, preferably in one or more fractions from one or more upper portions of the column, and the separated aldehydes and other oxygenated hydrocarbons are recovered in a separate fraction, preferably from a lower portion of the column. A majority of the added extractant (i.e., at least 50% of the amount added to the column) is also recovered from a lower portion of the column, preferably along with the recovered aldehydes.

**[0062]** In one embodiment of the invention, the separated aldehyde stream comprises at least a majority (i.e., at least 50%) of the aldehydes present in the provided olefin stream. Preferably, the separated aldehyde stream comprises at least about 75%, more preferably at least about 90%, of the aldehyde compounds present in the provided olefin stream.

**[0063]** In another embodiment of the invention, the stream containing the separated aldehyde product includes extractant. In one embodiment, the stream comprises at least about 50 wt % extractant, in another at least about 60 wt %, and

yet another at least about 70 wt %, based on total weight of the aldehyde containing stream. Preferably the extractant is methanol.

[0064] Other examples of oxygenated hydrocarbons which can be used as extractants, or mixed with the aldehyde stream and used as a pretreatment component, include those having a boiling point at 1 atm of from about 50°C to about 90°C. Preferred examples of such hydrocarbons include methanol, acetone, and methyl ethyl ketone.

[0065] In an optional embodiment of the invention, water is removed from the separated aldehyde stream prior to contact of the aldehyde composition with the molecular sieve in the pretreatment zone. Preferably, the aldehyde composition that is separated from the olefin product of the oxygenate conversion reaction is sent to a distillation type of process and at least a portion of the water in the aldehyde composition is removed. Desirably, the aldehyde stream that contacts the molecular sieve in the pretreatment zone comprises not greater than about 15 wt % water, based on total weight of the aldehyde stream injected into the pretreatment zone. Preferably the aldehyde stream that contacts the molecular sieve in the pretreatment zone comprises not greater than about 10 wt % water, more preferably not greater than about 5 wt % water, and most preferably not greater than about 1 wt % water, based on total weight of the aldehyde stream injected into the pretreatment zone.

#### IV. Pretreatment Conditions

[0066] According to the invention, fresh, regenerated, or a combination of fresh and regenerated molecular sieve is pretreated with the aldehyde composition in a pretreatment zone to form an integrated hydrocarbon co-catalyst within the porous framework of the molecular sieve. Effective pretreatment of the molecular sieve is obtained over a wide range of temperatures, pressures and space velocities. In general, the pretreatment temperature (i.e., the temperature in the pretreatment zone) is cooler than (i.e., less than) the oxygenate reaction temperature (i.e., the temperature in the oxygenate reaction zone). Desirably, the temperature in the pretreatment zone is at least 10°C less than that in the oxygenate reaction zone. Preferably, the temperature in the pretreatment zone is

at least 25°C, more preferably at least 50°C, and most preferably at least about 100°C less than that in the reaction zone.

**[0067]** In one embodiment, the temperature in the pretreatment zone is not greater than about 475°C. Preferably, the temperature in the pretreatment zone is not greater than about 425°C, and most preferably not greater than about 375°C.

**[0068]** In another embodiment, the temperature in the pretreatment zone is from about 150°C to about 475°C. Preferably, the temperature in the pretreatment zone is from about 200°C to about 425°C, more preferably from about 250°C to about 375°C.

**[0069]** Pretreatment of the molecular sieve is particularly effective on fresh, activated catalyst, or regenerated catalyst. Such catalyst is substantially low in total carbon content. As the fresh or regenerated catalyst contacts the aldehyde composition, the integrated hydrocarbon co-catalyst forms within the internal pore structure of the molecular sieve catalyst. In one embodiment, the molecular sieve that contacts the aldehyde composition to form the integrated hydrocarbon co-catalyst has a total carbon content of not greater than about 2 wt % prior to contact with the aldehyde composition. Preferably the molecular sieve catalyst that contacts the aldehyde composition has a total carbon content of not greater than about 1.5 wt %, more preferably not greater than about 1 wt %, and most preferably not greater than about 0.5 wt %, prior to contact with the aldehyde composition.

**[0070]** Following pretreatment, the molecular sieve contains the integrated hydrocarbon co-catalyst, which is a benzene type compound, within the various cages of the internal pore structure. In addition to using SSNMR to determine appropriate pretreatment of the molecular sieve, an additional embodiment involves measuring hydrocarbon content of the molecular sieve that has contacted the aldehyde composition. In one embodiment, the molecular sieve containing the integrated hydrocarbon co-catalyst has a hydrocarbon content of at least 0.1 wt %, preferably at least 1 wt %, more preferably at least about 5 wt %, and most preferably at least about 10 wt %, based on total weight of the molecular sieve, which excludes non-molecular sieve components such as binder, matrix, etc., which are optionally present in a catalyst composition.

**[0071]** In general, the molecular sieve that is being pretreated contacts the aldehyde composition in the pretreatment zone at a weight hourly space velocity (WHSV) that is lower than the WHSV of the molecular sieve contacting the oxygenate in the oxygenate reaction zone. In one embodiment, the molecular sieve contacts the aldehyde composition at a WHSV that is at least  $5 \text{ hr}^{-1}$  lower than that of the molecular sieve contacting the oxygenate in the oxygenate reaction zone. Preferably, the molecular sieve contacts the aldehyde composition at a WHSV that is at least about  $10 \text{ hr}^{-1}$ , more preferably at least about  $15 \text{ hr}^{-1}$  lower than that of the molecular sieve contacting the oxygenate in the oxygenate reaction zone.

**[0072]** In one embodiment, the molecular sieve and the aldehyde pretreatment composition contact one another in a pretreatment zone at a WHSV of from about  $5 \text{ hr}^{-1}$  to about  $200 \text{ hr}^{-1}$ . WHSVs in the lower range are preferred, particularly from about  $10 \text{ hr}^{-1}$  to about  $100 \text{ hr}^{-1}$ , and more particularly from about  $10 \text{ hr}^{-1}$  to about  $50 \text{ hr}^{-1}$ .

**[0073]** The pretreatment zone can be contained in a separate pretreatment zone or within a reactor vessel where the catalytic conversion of oxygenate to olefin takes place. In one embodiment, a separate pretreatment vessel is used. In a particular embodiment, the pretreatment vessel is an auxiliary fluidized bed reactor associated with the oxygenate conversion reactor and regenerator system. The auxiliary reactor is capable of continuously receiving catalyst from the regenerator and subsequently supplying pretreated catalyst to the oxygenate conversion reactor.

**[0074]** In another embodiment, pretreatment is carried out within the same vessel where the catalytic conversion of oxygenate to olefin product takes place. Preferably, two separate temperature zones are maintained to get proper introduction of hydrocarbon and formation of the integrated hydrocarbon co-catalyst. In one aspect, the molecular sieve to be pretreated is introduced into one zone along with the aldehyde composition to form the integrated hydrocarbon co-catalyst. Then, the pretreated molecular sieve containing the integrated hydrocarbon co-catalyst is sent to the other zone and contacted with oxygenate to convert the oxygenate to olefin product. Operating conditions in the two zones

are controlled for pretreatment and oxygenate reaction conditions. Either zone or both zones optionally includes heating or cooling equipment such as heat exchangers, steam coils, and cooling coils. In one embodiment, the pretreatment zone includes cooling equipment.

V. Converting Oxygenate to Olefins Using Pretreated Molecular Sieve

**[0075]** The molecular sieve pretreated with the aldehyde composition of this invention is contacted with oxygenate feedstock and the oxygenate is converted to olefin product. In a preferred embodiment of the process of the invention, the oxygenate feedstock contains one or more oxygenates, more specifically, one or more organic compound(s) containing at least one oxygen atom. In the most preferred embodiment of the process of this invention, the oxygenate in the feedstock is one or more alcohol(s), preferably aliphatic alcohol(s) where the aliphatic moiety of the alcohol(s) has from 1 to 20 carbon atoms, preferably from 1 to 10 carbon atoms, and most preferably from 1 to 4 carbon atoms. The alcohols useful as feedstock in the process of the invention include lower straight and branched chain aliphatic alcohols and their unsaturated counterparts.

**[0076]** Non-limiting examples of oxygenates include methanol, ethanol, n-propanol, isopropanol, methyl ethyl ether, dimethyl ether, diethyl ether, diisopropyl ether, formaldehyde, dimethyl carbonate, dimethyl ketone, acetic acid, and mixtures thereof.

**[0077]** In the most preferred embodiment, the feedstock is selected from one or more of methanol, ethanol, dimethyl ether, diethyl ether or a combination thereof, more preferably methanol and dimethyl ether, and most preferably methanol.

**[0078]** The various feedstocks discussed above, particularly a feedstock containing an oxygenate, more particularly a feedstock containing an alcohol, is converted primarily into one or more olefin(s). The olefin(s) produced from the feedstock typically have from 2 to 30 carbon atoms, preferably 2 to 8 carbon atoms, more preferably 2 to 6 carbon atoms, still more preferably 2 to 4 carbons atoms, and most preferably are ethylene and/or propylene.

**[0079]** Using the catalyst composition of the invention for the conversion of a feedstock, preferably a feedstock containing one or more oxygenates, the amount of olefin(s) produced based on the total weight of hydrocarbon produced is greater than 50 weight percent, typically greater than 60 weight percent, such as greater than 70 weight percent, and preferably greater than 75 weight percent. In one embodiment, the amount of ethylene and/or propylene produced based on the total weight of hydrocarbon product produced is greater than 65 weight percent, such as greater than 70 weight percent, for example greater than 75 weight percent, and preferably greater than 78 weight percent. Typically, the amount ethylene produced in weight percent based on the total weight of hydrocarbon product produced, is greater than 30 weight percent, such as greater than 35 weight percent, for example greater than 40 weight percent. In addition, the amount of propylene produced in weight percent based on the total weight of hydrocarbon product produced is greater than 20 weight percent, such as greater than 25 weight percent, for example greater than 30 weight percent, and preferably greater than 35 weight percent.

**[0080]** In a preferred embodiment of the invention, the oxygenate in the feedstock is converted at less than 100%. Generally, at less than 100% conversion, the quantity of aldehyde, particularly acetaldehyde, is greater in the olefin product stream. This means that at less than 100% conversion, more aldehyde can be recovered and used as a pretreatment stream, with the benefit being increased selectivity in the conversion process to ethylene and propylene, and less by-product formation of light by-products such as methane and heavier olefin products. Preferably, the oxygenate in the feedstock is converted at less than 100%, more preferably less than 99%, and most preferably less than 98%. It is desirable, however, to convert at least 85% of the oxygenate in the oxygenate feedstream, preferably at least 90%, and most preferably at least 95%.

**[0081]** In addition to the oxygenate component, such as methanol, the feedstock may contain one or more diluent(s), which are generally non-reactive to the feedstock or molecular sieve catalyst composition and are typically used to reduce the concentration of the feedstock. Non-limiting examples of diluents include helium, argon, nitrogen, carbon monoxide, carbon dioxide, water,

essentially non-reactive paraffins (especially alkanes such as methane, ethane, and propane), essentially non-reactive aromatic compounds, and mixtures thereof. The most preferred diluents are water and nitrogen, with water being particularly preferred.

[0082] The diluent, for example water, may be used either in a liquid or a vapor form, or a combination thereof. The diluent may be either added directly to the feedstock entering a reactor or added directly to the reactor, or added with the molecular sieve catalyst composition.

[0083] The olefin conversion process can be conducted over a wide range of temperatures, such as in the range of from about 200°C to about 1000°C, for example from about 250°C to about 800°C, including from about 250°C to about 750 °C, conveniently from about 300°C to about 650°C, typically from about 350°C to about 600°C and particularly from about 350°C to about 550°C.

[0084] Similarly, the olefin conversion process can be conducted over a wide range of pressures including autogenous pressure. Typically the partial pressure of the feedstock exclusive of any diluent therein employed in the process is in the range of from about 0.1 kPaa to about 5 MPaa, such as from about 5 kPaa to about 1 MPaa , and conveniently from about 20 kPaa to about 500 kPaa.

[0085] In the olefin conversion process, the weight hourly space velocity (WHSV), defined as the total weight of feedstock excluding any diluents per hour per weight of molecular sieve in the catalyst composition, typically ranges from about 1 hr<sup>-1</sup> to about 5000 hr<sup>-1</sup>, such as from about 2 hr<sup>-1</sup> to about 3000 hr<sup>-1</sup>, for example from about 5 hr<sup>-1</sup> to about 1500 hr<sup>-1</sup>, and conveniently from about 10 hr<sup>-1</sup> to about 1000 hr<sup>-1</sup>. In one embodiment, the WHSV is greater than 20 hr<sup>-1</sup> and, where feedstock contains methanol and/or dimethyl ether, is in the range of from about 20 hr<sup>-1</sup> to about 300 hr<sup>-1</sup>.

[0086] Where the olefin conversion process is conducted in a fluidized bed, the superficial gas velocity (SGV) of the feedstock including diluent and reaction products within the reactor system, and particularly within a riser reactor(s), is at least 0.1 meter per second (m/sec), such as greater than 0.5 m/sec, such as greater than 1 m/sec, for example greater than 2 m/sec, conveniently greater than 3 m/sec, and typically greater than 4 m/sec. See for example U.S.

Patent No. 6,552,240, the contents of which is fully incorporated herein by reference.

**[0087]** The olefin conversion process of the invention can be conducted as a fixed bed process. Preferably, the olefin conversion process is carried out as a fluidized bed process (including a turbulent bed process), such as a continuous fluidized bed process, and particularly a continuous high velocity fluidized bed process.

**[0088]** The process can take place in a variety of catalytic reactors such as hybrid reactors that have a dense bed or fixed bed reaction zones and/or fast fluidized bed reaction zones coupled together, circulating fluidized bed reactors, riser reactors, and the like. Suitable conventional reactor types are described in for example U.S. Patent No. 4,076,796, U.S. Patent No. 6,287,522 (dual riser), and *Fluidization Engineering*, D. Kunii and O. Levenspiel, Robert E. Krieger Publishing Company, New York, New York 1977, which are all herein fully incorporated by reference.

**[0089]** The preferred reactor types are riser reactors generally described in Riser Reactor, Fluidization and Fluid-Particle Systems, pages 48 to 59, F.A. Zenz and D.F. Othmo, Reinhold Publishing Corporation, New York, 1960, and U.S. Patent No. 6,166,282 (fast-fluidized bed reactor), and U.S. Patent Application Serial No. 09/564,613 filed May 4, 2000 (multiple riser reactor), which are all herein fully incorporated by reference.

**[0090]** In one practical embodiment, the process is conducted as a fluidized bed process or high velocity fluidized bed process utilizing a reactor system, a regeneration system and a recovery system.

**[0091]** In the olefin conversion process, the reactor system preferably includes a fluid bed reactor system having a first reaction zone within one or more riser reactor(s) and a second reaction zone within at least one disengaging vessel, typically comprising one or more cyclones. In one embodiment, the one or more riser reactor(s) and disengaging vessel are contained within a single reactor vessel. Fresh feedstock, preferably containing one or more oxygenates, optionally with one or more diluent(s), is fed to the one or more riser reactor(s) into which a molecular sieve catalyst composition or coked version thereof is introduced. In



one embodiment this invention, regenerated or fresh, uncoked catalyst, prior to being introduced to the riser reactor(s), is pretreated with the aldehyde composition of this invention, and then contacted with oxygenate feedstock to convert the oxygenate to olefin product at high selectivity to ethylene and propylene.

**[0092]** In another embodiment, oxygenate feedstock is fed to the olefin conversion reactor as a liquid and/or a vapor in a range of from 0.1 weight percent to about 99.9 weight percent, such as from about 1 weight percent to about 99 weight percent, more typically from about 5 weight percent to about 95 weight percent, based on the total weight of the feedstock including any diluent contained therein. The liquid and vapor feedstocks may be the same composition, or may contain varying proportions of the same or different feedstocks with the same or different diluents.

**[0093]** The feedstock entering the reactor system is preferably converted, partially or fully, preferably partially, in the first reactor zone into a gaseous effluent that enters the disengaging vessel along with the coked catalyst composition. In the preferred embodiment, cyclone(s) are provided within the disengaging vessel to separate the coked catalyst composition from the gaseous effluent containing one or more olefin(s) within the disengaging vessel. Although cyclones are preferred, gravity effects within the disengaging vessel can also be used to separate the catalyst composition from the gaseous effluent. Other methods for separating the catalyst composition from the gaseous effluent include the use of plates, caps, elbows, and the like.

**[0094]** In one embodiment, the disengaging vessel includes a stripping zone, typically in a lower portion of the disengaging vessel. In the stripping zone the coked catalyst composition is contacted with a gas, preferably one or a combination of steam, methane, carbon dioxide, carbon monoxide, hydrogen, or an inert gas such as argon, preferably steam, to recover adsorbed hydrocarbons from the coked catalyst composition that is then introduced to the regeneration system.

**[0095]** The coked catalyst composition is withdrawn from the disengaging vessel and introduced to the regeneration system. The regeneration system

comprises a regenerator where the coked catalyst composition is contacted with a regeneration medium, preferably a gas containing oxygen, under conventional regeneration conditions of temperature, pressure and residence time.

**[0096]** Non-limiting examples of suitable regeneration media include one or more of oxygen,  $O_3$ ,  $SO_3$ ,  $N_2O$ ,  $NO$ ,  $NO_2$ ,  $N_2O_5$ , air, air diluted with nitrogen or carbon dioxide, oxygen and water (U.S. Patent No. 6,245,703), carbon monoxide and/or hydrogen. Suitable regeneration conditions are those capable of burning coke from the coked catalyst composition, preferably to a level less than 0.5 weight percent based on the total weight of the coked molecular sieve catalyst composition entering the regeneration system. For example, the regeneration temperature may be in the range of from about 200°C to about 1500°C, such as from about 300°C to about 1000°C, for example from about 450°C to about 750°C, and conveniently from about 550°C to 700°C. The regeneration pressure may be in the range of from about 15 psia (103 kPaa) to about 500 psia (3448 kPaa), such as from about 20 psia (138 kPaa) to about 250 psia (1724 kPaa), including from about 25 psia (172kPaa) to about 150 psia (1034 kPaa), and conveniently from about 30 psia (207 kPaa) to about 60 psia (414 kPaa).

**[0097]** The residence time of the catalyst composition in the regenerator may be in the range of from about one minute to several hours, such as from about one minute to 100 minutes. The amount of oxygen in the regeneration flue gas (i.e., gas which leaves the regenerator) may be in the range of from about 0.01 mole percent to about 5 mole percent based on the total volume of the gas. The amount of oxygen in the gas used to regenerate the coked catalyst (i.e., fresh or feed gas) is typically at least about 15 mole percent, preferably at least about 20 mole percent, and more preferably from about 20 mole percent to about 30 mole percent, based on total amount of regeneration gas fed to the regenerator.

**[0098]** The burning of coke in the regeneration step is an exothermic reaction, and in an embodiment, the temperature within the regeneration system is controlled by various techniques in the art including feeding a cooled gas to the regenerator vessel, operated either in a batch, continuous, or semi-continuous mode, or a combination thereof. A preferred technique involves withdrawing the regenerated catalyst composition from the regeneration system and passing it

through a catalyst cooler to form a cooled regenerated catalyst composition. The catalyst cooler, in an embodiment, is a heat exchanger that is located either internal or external to the regeneration system. Other methods for operating a regeneration system are in disclosed U.S. Patent No. 6,290,916 (controlling moisture), which is herein fully incorporated by reference.

**[0099]** In one embodiment of the invention, the regenerated catalyst composition is withdrawn from the regeneration system and cooled using a catalyst cooler. The cooled catalyst is combined with a fresh molecular sieve catalyst composition and/or re-circulated molecular sieve catalyst composition and/or feedstock and/or fresh gas or liquids, and returned to the riser reactor(s). In one embodiment, the regenerated catalyst composition withdrawn from the regeneration system is returned to the riser reactor(s) directly, preferably after passing through a catalyst cooler. A carrier, such as an inert gas, feedstock vapor, steam or the like, may be used, semi-continuously or continuously, to facilitate the introduction of the regenerated catalyst composition to the reactor system, preferably to the one or more riser reactor(s). The regenerated catalyst is preferably pretreated with the aldehyde composition of this invention prior to combining with any unregenerated catalyst that is re-circulated from the reactor.

**[0100]** By controlling the flow of the regenerated catalyst composition that is being pretreated and the flow of any re-circulated and unregenerated catalyst that is to be combined with the pretreated catalyst composition, the optimum carbon content on the combined molecular sieve catalyst composition entering the reactor is maintained. Conventional techniques for controlling the flow of a catalyst composition described in Michael Louge, *Experimental Techniques, Circulating Fluidized Beds*, Grace, Avidan and Knowlton, eds., Blackie, 1997 (336-337), which is herein incorporated by reference.

**[0101]** Carbon or coke levels on the catalyst composition are measured by withdrawing the catalyst composition from the conversion process and determining its carbon content. Typical levels of coke on the molecular sieve catalyst composition, after regeneration, are in the range of from 0.01 weight percent to about 15 weight percent, such as from about 0.1 weight percent to about 10 weight percent, for example from about 0.2 weight percent to about 5 weight

percent, and conveniently from about 0.3 weight percent to about 2 weight percent based on the weight of the molecular sieve.

**[0102]** Gaseous effluent is withdrawn from the disengaging system and is passed through a recovery system to recover product and by-products, including the aldehyde pretreatment composition of this invention. Conventional recovery systems, techniques and sequences can be used in separating olefin(s) and purifying olefin(s) from the gaseous effluent. Conventional recovery systems generally comprise one or more or a combination of various separation, fractionation and/or distillation towers, columns, splitters, or trains, reaction systems such as ethylbenzene manufacture (U.S. Patent No. 5,476,978) and other derivative processes such as aldehydes, ketones and ester manufacture (U.S. Patent No. 5,675,041), and other associated equipment, for example various condensers, heat exchangers, refrigeration systems or chill trains, compressors, knock-out drums or pots, pumps, and the like.

**[0103]** Non-limiting examples of these towers, columns, splitters or trains used alone or in combination include one or more of a demethanizer, preferably a high temperature demethanizer, a dethanizer, a depropanizer, a wash tower often referred to as a caustic wash tower and/or quench tower, absorbers, adsorbers, membranes, ethylene (C<sub>2</sub>=) splitter, propylene (C<sub>3</sub>=) splitter and butene (C<sub>4</sub>=) splitter.

**[0104]** Various recovery systems useful for recovering olefin(s), such as ethylene, propylene and/or butene, are described in U.S. Patent No. 5,960,643 (secondary rich ethylene stream), U.S. Patent Nos. 5,019,143, 5,452,581 and 5,082,481 (membrane separations), U.S. Patent 5,672,197 (pressure dependent adsorbents), U.S. Patent No. 6,069,288 (hydrogen removal), U.S. Patent No. 5,904,880 (recovered methanol to hydrogen and carbon dioxide in one step), U.S. Patent No. 5,927,063 (recovered methanol to gas turbine power plant), and U.S. Patent No. 6,121,504 (direct product quench), U.S. Patent No. 6,121,503 (high purity olefins without superfractionation), and U.S. Patent No. 6,293,998 (pressure swing adsorption), which are all herein fully incorporated by reference.

**[0105]** Other recovery systems that include purification systems, for example for the purification of olefin(s), are described in *Kirk-Othmer*

*Encyclopedia of Chemical Technology, 4th Edition*, Volume 9, John Wiley & Sons, 1996, pages 249-271 and 894-899, which is herein incorporated by reference. Purification systems are also described in for example, U.S. Patent No. 6,271,428 (purification of a diolefin hydrocarbon stream), U.S. Patent No. 6,293,999 (separating propylene from propane), and U.S. Patent Application No. 09/689,363 filed October 20, 2000 (purge stream using hydrating catalyst), which are herein incorporated by reference.

**[0106]** Typically, in converting one or more oxygenates to olefin(s) having 2 or 3 carbon atoms, a minor amount hydrocarbons, particularly olefin(s), having 4 or more carbon atoms is also produced. The amount of C<sub>4</sub>+ olefins is normally less than 20 weight percent, such as less than 10 weight percent, for example less than 5 weight percent, and particularly less than 2 weight percent, based on the total weight of the effluent gas withdrawn from the process, excluding water. Typically, therefore the recovery system may include one or more reaction systems for converting the C<sub>4</sub>+ olefins to useful products.

**[0107]** Non-limiting examples of such reaction systems are described in U.S. Patent No. 5,955,640 (converting a four carbon product into butene-1), U.S. Patent No. 4,774,375 (isobutane and butene-2 oligomerized to an alkylate gasoline), U.S. Patent No. 6,049,017 (dimerization of n-butylene), U.S. Patent Nos. 4,287,369 and 5,763,678 (carbonylation or hydroformulation of higher olefins with carbon dioxide and hydrogen making carbonyl compounds), U.S. Patent No. 4,542,252 (multistage adiabatic process), U.S. Patent No. 5,634,354 (olefin-hydrogen recovery), and Cosyns, J. et al., *Process for Upgrading C3, C4 and C5 Olefinic Streams*, Pet. & Coal, Vol. 37, No. 4 (1995) (dimerizing or oligomerizing propylene, butylene and pentylene), which are all fully herein incorporated by reference.

**[0108]** The preferred light olefin(s) produced by any one of the processes described above are high purity ethylene and propylene products that contain the individual ethylene and propylene compounds in an amount greater than 80 percent, such as greater than 90 weight percent, such as greater than 95 weight percent, for example at least about 99 weight percent, based on the total weight of the product.

**[0109]** In one practical embodiment, the olefin forming process of the invention is integrated with one or more polyolefin processes to produce any one of a variety of polyolefins. (See, for example, U.S. Patent Application Serial No. 09/615,376 filed July 13, 2000, which is herein fully incorporated by reference.) In such an integrated process, at least one olefin in the olefin product stream, preferably ethylene or propylene, is separated and contacted with a polymerization catalyst to form a polyolefin product (e.g., polyethylene or polypropylene). The polyolefin product can be further treated as desired or shipped to other destinations for further treatment or processing.

**[0110]** Polymerization processes that can be integrated with the olefin conversion processes of this invention include solution, gas phase, slurry phase, high pressure processes, and combinations thereof. Particularly preferred is a gas phase or a slurry phase polymerization of one or more olefin(s) at least one of which is ethylene or propylene. These polymerization processes utilize a polymerization catalyst that can include any one or a combination of the molecular sieve catalysts discussed above. However, the preferred polymerization catalysts are the Ziegler-Natta, Phillips-type, metallocene, metallocene-type and advanced polymerization catalysts, and mixtures thereof.

**[0111]** In a preferred embodiment, the integrated process comprises a process for polymerizing one or more olefin(s) in the presence of a polymerization catalyst system in a polymerization reactor to produce one or more polymer products, wherein the one or more olefin(s) have been made by converting an alcohol, particularly methanol, using a molecular sieve catalyst composition as described above. The preferred polymerization process is a gas phase polymerization process and at least one of the olefins(s) is either ethylene or propylene, and preferably the polymerization catalyst system is a supported metallocene catalyst system. In this embodiment, the supported metallocene catalyst system comprises a support, a metallocene or metallocene-type compound and an activator, preferably the activator is a non-coordinating anion or alumoxane, or combination thereof, and most preferably the activator is alumoxane.

**[0112]** The polymers produced by the polymerization processes described above include linear low density polyethylene, elastomers, plastomers, high density polyethylene, low density polyethylene, polypropylene and polypropylene copolymers. The propylene based polymers produced by the polymerization processes include atactic polypropylene, isotactic polypropylene, syndiotactic polypropylene, and propylene random, block or impact copolymers.

VI. Examples of Separating Aldehyde from Olefin Streams

**[0113]** Two embodiments of separating aldehyde compounds from an olefin stream, particularly an olefin stream formed from an oxygenate feed stream are shown in FIGs. 1 and 2. FIG. 1 is a schematic showing separation of an aldehyde stream from the C<sub>2</sub>, C<sub>3</sub> and C<sub>4</sub> components of the olefin stream. FIG. 2 is a schematic showing separation of an aldehyde stream from the C<sub>2</sub>, C<sub>3</sub> and C<sub>4</sub> components of the olefin stream using an extractant to aid in removing the aldehyde compounds.

**[0114]** In the embodiment of FIG. 1, an oxygenate, methanol, is sent through a line 10 and contacted with aldehyde-pretreated metalloaluminophosphate molecular sieve catalyst in a reaction system 11, which includes a reactor and regenerator (not shown). The methanol is converted in the reaction system to olefin product, and the olefin product is sent through a line 12 to a separation system 13, which includes one or more distillation columns for separating the various olefin compounds into separate product streams. Preferably, the separation system 13 removes water from the olefin product stream in line 12 prior to separating the olefins into separate streams, since a substantial quantity of water is formed in the conversion of the methanol to olefin product.

**[0115]** According to the embodiment shown in FIG. 1, the separate product streams recovered in the separation system 13 include light end gases, ethylene (C<sub>2</sub>=), propylene (C<sub>3</sub>=) and butylene (C<sub>4</sub>=). In addition, a stream containing a majority of the aldehyde contained in the olefin product is separated in the separation system 13 and sent through a line 14 to a pretreatment zone 15.

**[0116]** In the pretreatment zone 15, regenerated catalyst that is sent from the regenerator in the reaction system 11 through a line 16 to the pretreatment zone 15 contacts the aldehyde stream, forming a pretreated catalyst. The

pretreated catalyst is then sent from the pretreatment zone 15 to the reaction system 11, by way of a line 17, to contact the methanol and form additional olefin product.

[0117] The embodiment in FIG. 2 is similar to the embodiment in FIG. 1, except that the embodiment in FIG. 2 includes the addition of an extractant, (e.g., methanol) to aid in separating the aldehyde in the separation system 23. In FIG. 2, the extractant is recovered in the separation system 24 along with the aldehyde and sent to a second (and optional) separation system 28, by way of a line 24. In the second, optional, separation system 28, water is removed from the aldehyde and extractant. The dewatered aldehyde and extractant stream are then sent through a line 29 to the pretreatment zone 25 to pretreat regenerated or fresh catalyst.

## VII. Examples of Pretreated Sieve

### Example 1

[0118] A mixture of 95 mg of formulated SAPO-34 catalyst and 1 g of 100- $\mu$ m silicon carbide was loaded into a microflow reactor made of 1/4" silicon steel tubing and equipped with a vaporizer for vaporizing the feed to the reactor. The reactor temperature was increased to 300°C while the catalyst was under helium flow (24 ml/min), and held for ca. 30 to 40 minutes for the temperature to stabilize.

[0119] The catalyst was pretreated by flowing 1 g acetaldehyde per gram of molecular sieve in the formulated catalyst through the reactor at 25 psig and at a WHSV of 88 hr<sup>-1</sup>. After the flow of acetaldehyde was stopped, 48 ml/min of helium was flowed through the reactor while the temperature was increased to 475°C. The flow was continued for about 45 minutes for the temperature to stabilize.

[0120] After the temperature was stabilized, methanol was injected for 6 to 10 minutes at 25 psig and at a WHSV of 100 hr<sup>-1</sup>. Effluent was collected using a 16-loop Valco valve. The effluent was analyzed using an on-line gas chromatograph (Hewlett Packard 6890) equipped with a flame ionization detector and a Q-column. The results are shown in Table 1. C<sub>1</sub>, C<sub>2</sub>=, C<sub>2</sub>°, C<sub>3</sub>=, C<sub>3</sub>°, C<sub>4</sub>S, C<sub>5</sub>+s, and C<sub>2+3</sub>= in the Table refer to methane, ethylene, ethane, propene, propane,



butenes and butanes, hydrocarbons that contain five or more than five carbons, and ethylene plus propene, respectively.

#### Example 2

**[0121]** The procedure of Example 1 was repeated, except that the catalyst was pretreated at a reactor temperature of 350°C. The results are shown in Table 1.

#### Example 3

**[0122]** The procedure of Example 1 was repeated, except that the catalyst was pretreated at a reactor temperature of 400°C. The results are shown in Table 1.

#### Example 4

**[0123]** The procedure of Example 1 was repeated, except that the catalyst was pretreated at a reactor temperature of 450°C. The results are shown in Table 1.

#### Example 5

**[0124]** The procedure of Example 1 was repeated, except that the catalyst was pretreated at a reactor temperature of 500°C. The results are shown in Table 1.

#### Example 6

**[0125]** The procedure of Example 1 was repeated, except that the catalyst was pretreated at a reactor temperature of 600°C. The results are shown in Table 1.

**Table 1**

<b>Pretreat Temp (°C)</b>	<b>C<sub>1</sub></b>	<b>C<sub>2</sub>=</b>	<b>C<sub>2</sub><sup>o</sup></b>	<b>C<sub>3</sub>=</b>	<b>C<sub>3</sub><sup>o</sup></b>	<b>C<sub>4</sub>s</b>	<b>C<sub>5</sub>+s</b>	<b>C<sub>2+3</sub>=</b>	<b>Life- time (g/g sieve)</b>	<b>C<sub>2</sub>= / C<sub>3</sub>=</b>
300	2.58	43.96	0.36	39.79	0.34	10.25	2.72	83.75	8.39	1.11
350	2.82	45.78	0.39	38.94	0.32	9.26	2.49	84.72	6.32	1.18
400	2.81	43.42	0.39	39.87	0.36	10.58	2.56	83.29	7.93	1.09
450	3.26	44.31	0.42	39.20	0.39	10.07	2.35	83.51	6.56	1.13
500	3.91	44.59	0.48	38.67	0.45	9.62	2.27	83.26	5.27	1.15
600	3.26	41.66	0.53	39.56	0.74	10.63	3.62	81.21	6.17	1.05

Example 7

[0126] Example 2 was repeated except that acetaldehyde was replaced with 1-butene as the pretreatment compound, and 1 g of 1-butene per gram of molecular sieve were injected. The pretreatment temperature of 350°C was selected, since that was the temperature that pretreatment of catalyst with acetaldehyde resulted in the highest selectivity to ethylene and propylene.

**Table 2**

Pretreat Temp (°C)	C <sub>1</sub>	C <sub>2</sub> =	C <sub>2</sub> <sup>o</sup>	C <sub>3</sub> =	C <sub>3</sub> <sup>o</sup>	C <sub>4</sub> s	C <sub>5</sub> +s	C <sub>2+3</sub> =	Life- time (g/g sieve)	C <sub>2</sub> = / C <sub>3</sub> =
350	1.54	37.44	0.29	39.87	0.58	13.87	5.48	77.30	18.48	0.94

[0127] Comparing the data of Table 1 to Table 2 shows that pretreating the molecular sieve with acetaldehyde results in a selectivity to ethylene and propylene that is substantially higher than that of 1-butene under substantially the same reaction conditions.

[0128] Having now fully described the invention, it will be appreciated by those skilled in the art that the invention may be performed within a wide range of parameters within what is claimed, without departing from the spirit and scope of the invention.